

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **06-158194**
 (43)Date of publication of application : **07.06.1994**

(51)Int.CI.

C22C 1/00
 B22F 7/02
 C01B 3/00
 C22C 14/00

(21)Application number : **04-312051**
 (22)Date of filing : **20.11.1992**

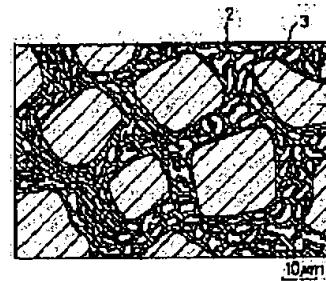
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(54) HYDROGEN OCCLUSION ALLOY MATERIAL

(57)Abstract:

PURPOSE: To raise the rate of absorption/emission of hydrogen by specifying the vol.% of a hydrogen occlusion alloy powder, the spongy porous body of carbon/graphite and the void produced therein.

CONSTITUTION: The hydrogen occlusion alloy material solidifying the hydrogen occlusion alloy powder performing absorption/emission of hydrogen reversibly and carbon/graphite is composed of 30-40vol.% hydrogen occlusion alloy powder 1, 20-30vol.% spongy porous body of carbon/graphite 2 surrounding the hydrogen occlusion alloy powder and 30-50vol.% void 3 produced in the spongy porous body. In this way, the heat conductivity and the rate of absorption/ emission of hydrogen are raised more than conventional method, and the hydrogen occlusion alloy powder is coated with carbon body, and also, desired shape can be shaped.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the hydrogen storing metal alloy material which hardened hydrogen storing metal alloy powder with carbon and the graphite in more detail about the hydrogen storing metal alloy which performs absorption and discharge of hydrogen in reversible.

[0002]

[Description of the Prior Art] If a hydrogen storing metal alloy is made into low temperature or high-pressure atmosphere together with hydrogen (H₂) gas, it will generate a metal hydride and will absorb hydrogen, and it generates heat, and conversely, if a metal hydride is made into an elevated temperature or low voltage atmosphere, it will emit hydrogen (separation). Research of such a hydrogen storing metal alloy and development are furthered, and use of the tank for hydrogen storage, heat pump, a nickel hydride battery, etc. is achieved.

[0003] However, in a hydrogen storing metal alloy, the function of property use equipment will fall remarkably by the pulverization resulting from the grid expansion and contraction by the fall of hydrogen absorption / discharge capacity by the contamination to the front face from atmosphere, and the recurrence of hydrogen absorption / discharge cycle. Moreover, since it is inferior to thermal conductivity, use independently is difficult when using as a heat carrier. Then, it was possible to form a carbon-deposit object in the front face of hydrogen storing metal alloy powder by the gaseous-phase depositing method so that these faults might be improved (for example, refer to JP,1-96301,A).

[0004]

[Problem(s) to be Solved by the Invention] There are the following problems in the method of forming a carbon-deposit object in such hydrogen storing metal alloy powder. First, piece [every] (every particle) independence of the hydrogen storing metal alloy powder which formed the carbon body in the front face by the gaseous-phase depositing method is achieved, respectively. ***** -- it comes out scatteringly as these fine particles, is, and does not have the configuration as the aggregate, and it cannot mold like clay without addition of caking additive In order to store the hydrogen storing metal alloy powder of a certain amount in the space of a certain configuration, the container of the configuration will be loaded with this powder. Furthermore, since deposition expands and contracts a hydrogen storing metal alloy about 20% by absorbing and emitting hydrogen, a device which a container absorbs volume change or is equal to volume change is made.

[0005] Moreover, in order to make a hydrogen storing metal alloy absorb and emit hydrogen, you have to cool and heat this alloy. Then, it is necessary to prepare the mechanisms for cooling and heating (the pipe for heat carriers, thermolysis, the fan for endothermics, etc.) in the container which held hydrogen storing metal alloy powder. A tare will become heavy if it has such a mechanism. For example, in the case of the container for stationary-type hydrogen storage, it is 3 50Nm of hydrogen quantities to be stored. It is said that the container of ** serves as 100kg of numbers from dozens of kg.

[0006] Furthermore, the thermal conductivity of this powder at the time of filling up a container with the hydrogen storing metal alloy powder to a front face which has not carried out carbon-deposit processing is about 1-3 W/mK, and is quite metal / of copper (thermal conductivity : about 300 W/mK) and aluminum (thermal conductivity : about 150 W/mK) / alumina ceramics (thermal conductivity : about 30 W/mK),] a low. The thermal conductivity of the hydrogen storing metal alloy powder with which it was only in contact between powder, and was filled up although the thermal conductivity of fine particles was considerably raised by the thermal conductivity (about 100 to 150 W/mK) of a carbon body when it was the hydrogen storing metal alloy powder which deposited the carbon body on the front face like an above-mentioned proposal is 10 - 30 W/mK and] still a low. For this reason, rate controlling of the absorption / discharge speed of the hydrogen in this case is carried out by heat conduction of a hydrogen storing metal alloy powder restoration object.

[0007] The purpose of this invention is offering the hydrogen storing metal alloy powder-molding object molded in the desired configuration, and is raising the thermal conductivity of this Plastic solid, and hydrogen absorption / discharge speed conventionally further at the same time it covers hydrogen storing metal alloy powder with a carbon body in consideration of the trouble mentioned above.

[0008]

[Means for Solving the Problem] The above-mentioned purpose is attained by the hydrogen storing metal alloy material characterized by the bird clapper from the opening of 30 produced on the spongy porosity object of the carbon and the graphite of 20 which encloses the hydrogen storing metal alloy powder and this hydrogen storing metal alloy powder of 30 - 40 volume % - 30 volume %, and this spongy porosity object - 50 volume %.

[0009] Carbon and a graphite fiber can be formed into 20-30 deposition % composite into this hydrogen storing metal alloy material, and fiber strengthening can raise intensity.

[0010]

[Function] Carbon and the graphite layer 2 cover the hydrogen storing metal alloy powder 1, and the structure of the hydrogen storing metal alloy material concerning the invention in this application is the structure where this carbon and graphite layer 2 are porosity, and is sponge-like (sponge) as a whole, and spongy carbon and 3-dimensional graphite porosity object enclose hydrogen storing metal alloy powder, as shown in drawing 1. Elastic deformation is possible for this porosity object, it suppresses the cubical expansion and contraction of the powder accompanying absorption and discharge of hydrogen, and suppresses and prevents the powdered decay phenomenon (pulverization) in which this originates in cubical expansion and contraction, and happens. And carbon and the graphite porosity object 2 have an opening (foam) 3, and the opening has not been independent completely, and **** which is open for free passage by somewhere (continuation), and hydrogen gas can pass this hydrogen storing metal alloy material easily by passing along the opening 3 of this porosity object 2.

[0011] Fe-Ti by which hydrogen storing metal alloy powder is known conventionally A system alloy and Fe-Mn A system alloy and Zr-nickel A system alloy and Te-Zr pass a well-known powder manufacturing process (raw material combination, the dissolution, casting, heat treatment, trituration) using a stable alloy chemically to about 1200 degrees C, such as a system alloy, -- it is made 10-30 micrometers of mean particle diameters If there is less hydrogen storing metal alloy powder than 30 volume %, absorption and emission efficiency of hydrogen will become so small, it becomes inadequate, and on the other hand, if [than 40 volume %] more, the state where alloys touch will increase, the flow and heat conduction of hydrogen gas will become bad, and absorption / discharge speed of the hydrogen accompanied by a temperature change will become slow (that is, responsibility becomes bad).

[0012] If carbon and a graphite porosity object are formed of carbonization and graphitization of a petroleum pitch, takes 20 volume % to constitute the spongy gestalt and to secure predetermined voidage and exceeds 30 volume % so that it may mention later, it will lower the amount of hydrogen storing metal alloy powder, and voidage. In case carbon and a graphite porosity object are formed, the opening (foam) is formed using the resin chip which works as a binder and volatilizes at an elevated temperature, and, as for voidage, it is desirable that it is 30 to 50 whole volume %. The opening has influenced thermal conductivity and the gas transmission rate, thermal conductivity falls with the increase in voidage, and a gas transmission rate becomes quick conversely. Moreover, thermal conductivity, and a gas transmission rate and hydrogen rate of absorption are in a positive correlation. From these things, it finds out that this invention person is about 40 volume % from an experiment about the voidage from which hydrogen rate of absorption becomes the maximum, and it is suitable if it is this **10 volume % extent. A low and a gas transmission rate become [voidage] slow rather than 30 volume %, and on the other hand, if 50 volume % is exceeded, thermal conductivity will become low.

[0013] Furthermore, it is dependent on the configuration of the resin chip to be used, an average diameter is 1-3 micrometers, and the configuration of an opening has the desirable opening produced using the detailed pillar-like chip whose length is 4-9 micrometers. In the opening corresponding to less than 1 micrometer in a chip diameter, an opening tends to become independent, respectively and a gas transmission rate becomes easy to become slow. On the other hand, in the opening corresponding to a larger thing than 3 micrometers, the hydrogen storing metal alloy by hydrogen absorption / discharge recurrence comes to carry out pulverization. The continuous opening is too large, rigidity becomes low, and since the work which reduces expansion and contraction of this alloy by hydrogen absorption and discharge was lost, this is considered. Moreover, when the aspect ratio of an opening is two to about six, hydrogen rate of absorption is comparatively high, the opening length corresponding to a resin length of tip falls in except [it], and its length corresponding to a chip length of 4-9 micrometers is desirable.

[0014]

[Example] Hereafter, with reference to an accompanying drawing, the example of an embodiment and the example of comparison of this invention explain this invention in detail.

As the hydrogen storing metal alloy material concerning example 1 this invention was shown in drawing 2, it manufactured as follows.

[0015] (a) The Fe-Ti hydrogen storing metal alloy powder of 20-30 micrometers of mean particle diameters was prepared first. For that purpose, weighing capacity of iron (Fe) powder and the titanium (Ti) powder was carried out so that a weight ratio might be set to 1:1, and it mixed in the agate mortar, this mixed powder was dissolved and cast in the argon arc fusion furnace, and the button head-like Fe-Ti alloy lump was manufactured. Equalization heat treatment was performed within the vacuum heating furnace, and milling equipment ground this alloy lump to predetermined particle size, and he was made into fine particles.

[0016] (b) The polyester chip (average diameter : 2 micrometers, average length : 8 micrometers) was prepared as the petroleum pitch (viscous fluid like a coal tar) which is the raw material of carbon and a graphite porosity object, and a resin which will form an opening. Weighing capacity of a petroleum pitch and the polyester chip was carried out so that a volume ratio might be set to 3:4:3, and they were carried out mixture and **** with the nylon ball mill in the end of an alloy powder. The thing with a diameter [of 10cm] x length of 20cm was used for the mill container, the thing with a diameter of 4mm was used for the ball, and grade mixture was carried out one whole day and night.

[0017] (c) Mixed powder was supplied to the attached stirrer of an injection molding machine, and it stirred, heating at 200 degrees C. And this was injected to the metal mold of a predetermined configuration with the injection molding machine, and the sample (mold goods) was created. This sample was 40mm in diameter [of 40mm] x length.

(d) In the elevated-temperature furnace, in air, the sample (mold goods) was heated at 300 degrees C, and was held for 2 hours. Thereby, it pyrolyzes namely, oxidizes, the polymerization of a nitrile group and the oxidization of aliphatic carbon which are included in a petroleum pitch take place, and a petroleum pitch and a polyester chip call this process stabilization. [0018] (e) Then, the inside of an elevated-temperature furnace was replaced by nitrogen-gas-atmosphere mind, the temperature up was carried out to 400 degrees C, it held for 2 hours, the temperature up was further carried out to 1000 degrees C, and it held for 2 hours. Sublimation removal of the stable polyester chip was decomposed and carried out by this, the opening section was formed, and on the other hand, atoms, such as oxygen, hydrogen, and nitrogen, carried out separation secession, carbon remained, and the stable petroleum chip was graphitized in part, and formed carbon and the graphite porosity object 2 (drawing 1). The hydrogen storing metal alloy material (voidage : 40 volume %) which has structure as shown in drawing 1 by such carbonization processing was manufactured.

[0019] (f) This hydrogen storing metal alloy material was inserted in the hydrogen storage container made from stainless steel, and was sealed. And in order that hydrogen might make it easy to frequent a hydrogen storing metal alloy easily, the hydrogen absorption in ten atmospheric pressure and the hydrogen desorption in 0.5 atmospheric pressure (reduced pressure) were repeated 10 times. This processing is called activation.

What covered the carbon body with the gaseous-phase depositing method as proposed by this in JP,1-96301,A was prepared using the Fe-Ti hydrogen storing metal alloy powder manufactured in an above-mentioned process (a) as an example 1 of comparison. Furthermore, Fe-Ti hydrogen storing metal alloy powder as it is was used without carrying out covering like this invention or the gaseous-phase depositing method as an example 2 of comparison. It loaded with each powder so that it might become an amount in the same end of an alloy powder as the same hydrogen storage container made from stainless steel in a process (mosquito).

[0020] The thermal conductivity is 50 - 80 W/mK, and the hydrogen storing metal alloy material which has the carbon and the 3-dimensional graphite porosity object concerning this invention manufactured at the process mentioned above became high also 2.5 to 5 times rather than the thermal conductivity in the case of being the example 2 of comparison (10 - 30 W/mK). At the time of hydrogen absorption, temperature was made into 30 degrees C for hydrogen absorption / discharge speed about the hydrogen storing metal alloy powder of the hydrogen storing metal alloy material of this invention, the example 1 of comparison, and the example 2 of comparison with the hydrogen storage container made from stainless steel, and the pressure was made into 25 atmospheric pressure, and temperature was made into 60 degrees C at the time of hydrogen desorption, and the pressure was made into one atmospheric pressure and measured. The water jacket was formed in the exterior of the hydrogen storage container made from stainless steel, and when cold water or warm water supplied, the hydrogen storing metal alloy was cooled and heated. the measurement result -- a vertical axis -- a hydrogen absorption (discharge) velocity ratio -- and it is shown in drawing 3 which set the horizontal axis as time In drawing 3 , it is the case where a thick line A is the hydrogen storing metal alloy material of this invention, is the case where a thin line B is the example 1 of comparison, and is the case where a dashed line C is the example 2 of comparison. The hydrogen storing metal alloy material of this invention has the quickest speed of absorption and discharge of hydrogen so that drawing 3 may show. This result is in agreement with the order of the size of thermal conductivity, and improvement in heat electric conductivity is considered to be the key factor of an improvement of the occlusion and discharge speed of hydrogen.

[0021] In order to investigate the influence of the hydrogen rate of absorption on the impurity gas contained in hydrogen, the hydrogen rate of absorption of the case of a high grade and the case of impurity (4000 ppm) content was measured the condition at the time of above-mentioned hydrogen absorption about the hydrogen storing metal alloy material of this invention, and the unsettled hydrogen storing metal alloy powder of the example 2 of comparison. The measurement result is shown in drawing 4 . It is the case where a solid line A is the hydrogen storing metal alloy material of this invention, and is the case where a dashed line C is the example 2 of comparison. Although hydrogen rate of absorption will become slow if impurity gas exists so that drawing 4 may show, the hydrogen storing metal alloy material of this invention has the rate of absorption of hydrogen quicker than the example 2 of comparison. Carbon and a graphite porosity object work as a filter of impurity gas, and this is considered to have avoided poisoning of hydrogen storing metal alloy powder.

[0022] The rate of the same hydrogen storing metal alloy powder as the case of example 2 example 1, a petroleum pitch and **** for a polyester chip, and hydrogen storing metal alloy powder was considered as 30 volume % regularity, by changing the amount of a polyester chip (diameter : 2 micrometers, length : 8 micrometers) and a petroleum pitch, voidage was fluctuated in the range of 10 - 60 volume %, and hydrogen storing metal alloy material was manufactured by the manufacture method in an example 1. Hydrogen rate of absorption (30 degrees C, H2 gas pressure of 25 atmospheric pressure), thermal conductivity, and a gas transmission rate are measured about each hydrogen storing metal alloy material, and the result is shown in drawing 5 . In addition, hydrogen rate of absorption is the speed at the time of a hydrogen absorption start, and is equivalent to the standup inclination of the hydrogen rate-of-absorption ratio in drawing 3 . Moreover, in drawing 5 , it is the value (R/Rav60:%) standardized by the gas transmission rate in voidage 60 volume % as a gas transmission-rate ratio.

[0023] Thermal conductivity becomes small although a gas transmission rate becomes large as voidage becomes large so that drawing 5 may show. And hydrogen rate of absorption is changed so that the highest mountain type curve near the 40 volume % may be drawn. It sees synthetically and 30 - 50 volume % of voidage is especially desirable in consideration of hydrogen rate of absorption.

The rate of the same hydrogen storing metal alloy powder as the case of example 3 example 1 and a petroleum pitch, **** for a polyester chip which changed the configuration as follows, hydrogen storing metal alloy powder and a petroleum pitch, and a polyester chip was considered as 30 volume %, 30 volume %, and 40 volume % regularity, and hydrogen storing metal alloy

material was manufactured by the manufacture method in an example 1.

[0024] The average-diameter (micrometer) x length of a polyester chip (micrometer): 1 x 42 x 8 (example 1) 3 x124 x16 -- about each hydrogen storing metal alloy material, absorption and discharge of hydrogen were made into 30 degrees C and 25 atmospheric pressure like the example 1 at the time of hydrogen absorption, this was repeated 100 times as 60 degrees C and one atmospheric pressure at the time of hydrogen desorption, and the first time and the 100th hydrogen rate of absorption were measured The result shown in drawing 6 by making the measured value into a hydrogen rate-of-absorption ratio was obtained having used as 100 hydrogen rate of absorption in the case where average diameter x length is 2micrometerx8micrometer. The time of the average diameter (2 micrometers) of a polyester chip is [in 100 times of absorption discharge recurrence] the quickest at hydrogen rate of absorption so that clearly from drawing 6 . Moreover, when an average diameter exceeds 3 micrometers, the pulverization in the end of an alloy powder may arise by the absorption discharge recurrence of hydrogen. This will be because the opening was too large and it became impossible to reduce expansion and contraction of a hydrogen storing metal alloy.

[0025] Furthermore, the result which shows it to drawing 7 when the obtained measured value is arranged on the basis of the aspect ratio (namely, aspect ratio of a polyester chip) of an opening is obtained. In this case, it is the quickest, and using this as 100, the hydrogen rate of absorption at the time of a chip (diameter : 2 micrometers, length : 8 micrometers, an aspect ratio : 4) converts measured value, and is shown. 2-6, then hydrogen rate of absorption are comparatively high in an aspect ratio, and if out of range, this thing [falling] is understood.

[0026] Although the petroleum pitch and the polyester chip are used in the example mentioned above, it is also possible to use a coal tar, a plastics chip, etc.

[0027]

[Effect of the Invention] As explained above, the hydrogen storing metal alloy material concerning this invention enclosed the hydrogen storing metal alloy powder of each [the carbon and the graphite porosity object which has an opening], has offered the predetermined configuration, can suppress pulverization, and can raise thermal conductivity, and can also raise hydrogen absorption / discharge speed. Furthermore, although the cubical expansion and the amount of contraction distortion of hydrogen storing metal alloy powder are as large as 20%, since a powdered particle size is as small as 10-30 micrometers, deformation is as small as 2-6 micrometers, the spongy porosity object of the elastic body which has an opening will absorb this deformation, and the deformation as the hydrogen storing metal alloy material (Plastic solid) itself is very small. The stress load to a container is avoidable by preparing the crevice of deformation between hold containers, even if deformation arises into the hydrogen storing metal alloy material itself. And it is made whether carbon and a graphite are right conductors, and energization heating is directly possible for it, and it is simple in the heating means at the time of hydrogen desorption. From these things, a container should just make a container from the minimum board thickness for it that what is necessary is just to have the function which only shuts up hydrogen. It follows, for example, in the case of the container for stationary-type hydrogen storage, is 3 50Nm of hydrogen quantities to be stored. Lightweight-ization of the container of ** is attained to about several kg.

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(11) Publication number: **06158194 A**

(43) Date of publication of application: **07 . 06 . 94**

(51) Int. Cl

C22C 1/00
B22F 7/02
C01B 3/00
C22C 14/00

(21) Application number: **04312051**

(71) Applicant: **TOYOTA MOTOR CORP**

(22) Date of filing: **20 . 11 . 92**

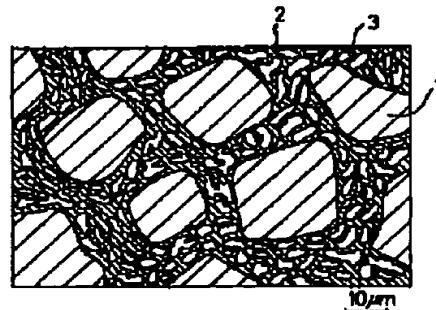
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(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平6-158194

(43)公開日 平成6年(1994)6月7日

(51)Int.Cl.⁶

識別記号

庁内整理番号

F I

技術表示箇所

C 22 C 1/00

C

B 22 F 7/02

C 01 B 3/00

B

C 22 C 14/00

A

審査請求 未請求 請求項の数1(全6頁)

(21)出願番号

特願平4-312051

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(22)出願日 平成4年(1992)11月20日

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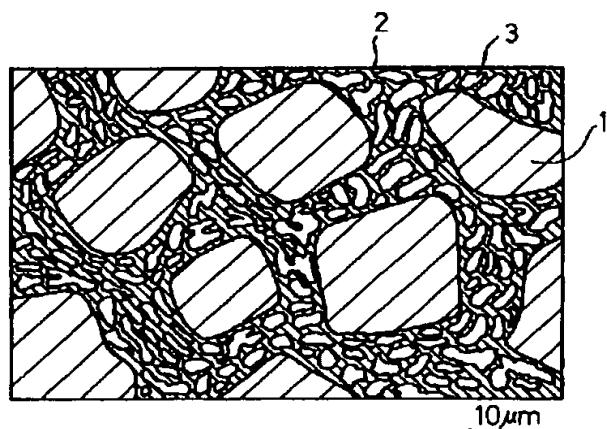
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(54)【発明の名称】 水素吸蔵合金材料

(57)【要約】

【目的】 水素の吸収・放出を可逆的に行う水素吸蔵合金粉末を炭素・黒鉛で固めた水素吸蔵合金材料に関し、熱伝導率および水素吸収・放出速度を従来よりも高め、かつ水素吸蔵合金粉末を炭素体で被覆すると同時に所望の形状に造形した水素吸蔵合金粉末成形体を提供する。

【構成】 30～40体積%の水素吸蔵合金粉末1と、該水素吸蔵合金粉末を取り囲んでいる20～30体積%の炭素・黒鉛の海綿状多孔質体2と、該海綿状多孔質体に生じる30～50体積%の空隙3とからなるように水素吸蔵合金材料を構成する。



1…水素吸蔵合金粉末

2…炭素・黒鉛多孔質体(層)

3…空隙

【特許請求の範囲】

【請求項1】 30～40体積%の水素吸蔵合金粉末(1)と、該水素吸蔵合金粉末を取り囲んでいる20～30体積%の炭素・黒鉛の海綿状多孔質体(2)と、該海綿状多孔質体に生じる30～50体積%の空隙(3)とからなることを特徴とする水素吸蔵合金材料。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、水素の吸収・放出を可逆的に行う水素吸蔵合金に関し、より詳しくは、水素吸蔵合金粉末を炭素・黒鉛で固めた水素吸蔵合金材料に関する。

【0002】

【従来の技術】水素吸蔵合金は、水素(H₂)ガスと一緒に低温または高圧雰囲気にすると金属水素化物を生成して水素を吸収し、かつ発熱し、逆に、金属水素化物を高温または低圧雰囲気にすると、水素を放出(分離)する。このような水素吸蔵合金の研究、開発が進められ、水素貯蔵用タンク、ヒートポンプ、ニッケル-水素電池などの利用が図られている。

【0003】しかしながら、水素吸蔵合金においては、雰囲気からの表面への汚染による水素吸収・放出能力の低下、および水素吸収・放出サイクルの繰返しによる格子膨張・収縮に起因した微粉化によって特性利用装置の機能が著しく低下してしまう。また、熱伝導性に劣るために、熱媒体として利用する場合には、単独での使用は難しい。そこで、これらの欠点を少しでも改善するように、水素吸蔵合金粉末の表面に気相堆積法によって炭素堆積物を形成することが考えられた(例えば、特開平1-96301号公報参照)。

【0004】

【発明が解決しようとする課題】このような水素吸蔵合金粉末に炭素堆積物を形成する方法には、以下の問題がある。先ず、気相堆積法で炭素体を表面に形成した水素吸蔵合金粉末は、それぞれ一個ずつ(粒子毎に)独立している。したがって、これら粉体としてばらばらであり、集合体としての形状を有していないし、粘結材の添加がなければ、粘土のように造形できない。ある量の水素吸蔵合金粉末をある形状の空間に収めるためには、その形状の容器に該粉末を装填することになる。さらに、水素吸蔵合金は水素を吸収・放出することにより、堆積が約20%も膨張・収縮するので、容器は体積変動を吸収するかあるいは体積変動に耐えるような工夫がなされている。

【0005】また、水素吸蔵合金に水素を吸収・放出させるためには、該合金を冷却・加熱しなければならない。そこで、水素吸蔵合金粉末を収容した容器に、冷却・加熱のための機構(熱媒体用パイプ、放熱・吸熱用ファンなど)を設ける必要がある。このような機構を備えると、容器重量は重くなってしまう。例えば、定置式水

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素貯蔵用容器の場合に、水素貯蔵量50Nm³用の容器は数十kgから数百kgとなると言われている。

【0006】さらに、表面への炭素堆積処理していない水素吸蔵合金粉末を容器に充填した場合の該粉末の熱伝導率は1～3W/mK程度であり、アルミニナセラミックス(熱伝導率:約30W/mK)や、銅(熱伝導率:約300W/mK)、アルミニウム(熱伝導率:約150W/mK)の金属などよりもかなり低い。上述の提案のように表面に炭素体を堆積した水素吸蔵合金粉末であれば、炭素体の熱伝導率(約100～150W/mK)によって粉体の熱伝導率はかなり高められるものの、粉末間は単に接触しているだけであり、充填した水素吸蔵合金粉末の熱伝導率は10～30W/mKとまだ低い。このために、この場合の水素の吸収・放出速度は水素吸蔵合金粉末充填体の熱伝導により律速される。

【0007】本発明の目的は、上述した問題点を考慮して、水素吸蔵合金粉末を炭素体で被覆すると同時に所望の形状に造形した水素吸蔵合金粉末成形体を提供することであり、さらに、該成形体の熱伝導率および水素吸収・放出速度を従来よりも高めることである。

【0008】

【課題を解決するための手段】上述の目的が、30～40体積%の水素吸蔵合金粉末と、該水素吸蔵合金粉末を取り囲んでいる20～30体積%の炭素・黒鉛の海綿状多孔質体と、該海綿状多孔質体に生じる30～50体積%の空隙とからなることを特徴とする水素吸蔵合金材料によって達成される。

【0009】この水素吸蔵合金材料に炭素・黒鉛繊維を20～30堆積%複合化することができ、繊維強化によって強度を高めることができる。

【0010】

【作用】本願発明に係る水素吸蔵合金材料は、その構造が図1に示すように、水素吸蔵合金粉末1を炭素・黒鉛層2が覆い、該炭素・黒鉛層2が多孔質であって全体として海綿(スポンジ)状であり、水素吸蔵合金粉末を海綿状の炭素・黒鉛3次元多孔質体が取り囲んでいる構造である。この多孔質体は弾性変形可能であり、水素の吸収・放出に伴う粉末の体積膨張・収縮を抑制し、このことが体積膨張・収縮に起因して起こる粉末の崩壊現象(微粉化)を抑制・防止する。そして、炭素・黒鉛多孔質体2は空隙(気泡)3を有しあつ空隙は完全に独立しているのではなくて、どこかで連通(連続)しているので、水素ガスは該多孔質体2の空隙3を通ることで該水素吸蔵合金材料を容易に通過することができる。

【0011】水素吸蔵合金粉末は、従来より知られているFe-Ti系合金、Fe-Mn系合金、Zr-Ni系合金、Te-Zr系合金などの1200℃程度まで化学的に安定な合金を用い、公知の粉末製造工程(原料配合、溶解、鋳造、熱処理、粉碎)を経て平均粒径10～30μmにしたものである。水素吸蔵合金粉末が30体積%より少ないと、

水素の吸収・放出効果がそれだけ小さくなり、不十分となり、一方、40体積%より多いと、合金どうしが接触している状態が増え、水素ガスの流れや熱伝導が悪くなり、温度変化を伴う水素の吸収・放出速度がおそくなる（即ち、応答性が悪くなる）。

【0012】炭素・黒鉛多孔質体は後述するように、石油ピッチの炭化・黒鉛化によって形成されるものであり、その海綿状形態を構成しつつ所定の空隙率を確保するのに20体積%を要し、30体積%を越えると、水素吸収合金粉末量および空隙率を下げることになってしまいます。炭素・黒鉛多孔質体を形成する際に、バインダーとして働きつつ高温で揮発する樹脂チップを用いて空隙（気泡）を形成しており、空隙率は全体の30～50体積%であるのが好ましい。空隙は熱伝導率、ガス透過速度に影響しており、空隙率の増加に伴い熱伝導率は低下し、逆にガス透過速度は速くなる。また、熱伝導率およびガス透過速度と水素吸収速度とは正の相関関係にある。これらのことから、水素吸収速度が最大になる空隙率を本発明者は実験から約40体積%であることを見出し、この±10体積%程度であれば適切である。空隙率が30体積%よりも低いと、ガス透過速度が遅くなり、一方、50体積%を越えると、熱伝導率が低くなる。

【0013】更に、空隙の形状は使用する樹脂チップの形状に依存するわけであり、平均直径が1～3μmで、長さが4～9μmの微細な円柱状チップを用いて生じた空隙が好ましい。チップ直径が1μm未満に対応する空隙では、空隙がそれぞれ独立しやすく、ガス透過速度が遅くなりやすくなる。一方、3μmよりも大きいものに対応する空隙では、水素吸収・放出繰返しによる水素吸収合金が微粉化するようになる。これは、連続した空隙が大きすぎて剛性が低くなり、水素吸収・放出による該合金の膨張・収縮を低減する働きがなくなったためと、考えられる。また、樹脂チップの長さに対応する空隙長さは、空隙のアスペクト比が2～6程度の場合に水素吸収速度が比較的高く、それ以外では低下し、チップ長さ4～9μmに対応する長さが好ましい。

【0014】

【実施例】以下、添付図面を参照して、本発明の実施態様例および比較例によって本発明を詳細に説明する。

実施例1

本発明に係る水素吸収合金材料を図2に示した如く次のようにして製造した。

【0015】（ア）先ず、平均粒径20～30μmのFe-Ti水素吸収合金粉末を用意した。そのためには、鉄（Fe）粉末とチタン（Ti）粉末とを重量比が1:1になるように秤量し、メノウ乳鉢中で混合し、この混合粉をアルゴンアーク溶解炉にて溶解・鋳造して、ボタンヘッド状のFe-Ti合金塊を製作した。この合金塊を真空加熱炉内で均一化熱処理を施し、それからミリング装置によって所定粒径に粉碎して粉体とした。

【0016】（イ）炭素・黒鉛多孔質体の原料である石油ピッチ（コールタールのような粘性流体）と、空隙を作ることになる樹脂としてポリエステルチップ（平均直径：2μm、平均長さ：8μm）とを用意した。合金粉末、石油ピッチおよびポリエステルチップを体積比が3:4:3になるように秤量し、ナイロンボールミルによって混合・混粉した。ミル容器には直径10cm×長さ20cmのものを、ボールには直径4mmのものを使用し、1昼夜程度混合した。

10 【0017】（ウ）射出成形機の付属搅拌器に混合粉を投入し、200℃に加熱しながら搅拌した。そして、これを射出成形機によって所定形状の金型へ射出し、試料（成形品）を作成した。この試料は直径40mm×長さ40mmであった。

（エ）試料（成形品）を高温炉において、空气中で300℃に加熱し、2時間保持した。これにより、石油ピッチおよびポリエステルチップは熱分解すなわち酸化し、石油ピッチに含まれるニトリル基の重合と脂肪族炭素の酸化が起こり、この工程を安定化と呼ぶ。

20 【0018】（オ）続いて、高温炉内を窒素雰囲気に置換し、400℃に昇温し、2時間保持し、さらに、1000℃に昇温し、2時間保持した。これにより、安定化されたポリエステルチップは分解して昇華除去され、空隙部を形成し、一方、安定化された石油チップは酸素、水素、窒素などの原子が分離離脱し、炭素が残留し、一部黒鉛化して、炭素・黒鉛多孔質体2（図1）を形成した。このような炭化処理によって、図1に示すような構造を有する水素吸収合金材料（空隙率：40体積%）を製造した。

30 【0019】（カ）この水素吸収合金材料をステンレス製水素貯蔵容器に挿入し、密閉した。そして、水素吸収合金に水素が容易に出入りし易くするために、10気圧での水素吸収と0.5気圧（減圧）での水素放出を10回繰り返した。この処理を活性化と呼ぶ。

比較例1として、上述の工程（ア）にて製造したFe-Ti水素吸収合金粉末を用いて、これに特開平1-96301号公報にて提案されたように気相堆積法によって炭素体を被覆したものを用意した。さらに、比較例2として、本発明あるいは気相堆積法のように被覆すること

40 をしないで、そのままのFe-Ti水素吸収合金粉末を用いた。それぞれの粉末を工程（カ）での同じステンレス製水素貯蔵容器に同じ合金粉末量になるように装填した。

【0020】上述した工程で製造した本発明に係る炭素・黒鉛3次元多孔質体を有する水素吸収合金材料は、その熱伝導率が50～80W/mKであり、比較例2の場合の熱伝導率（10～30W/mK）よりも2.5～5倍も高くなかった。本発明の水素吸収合金材料、比較例1および比較例2の水素吸収合金粉末についての水素吸収・放出速度をステンレス製水素貯蔵容器で、水素吸収時には温度を

30°Cとし、圧力を25気圧とし、また、水素放出時には温度を60°Cとし、圧力を1気圧とし測定した。ステンレス製水素貯蔵容器の外部に水ジャケットを設けて、冷水または温水の供給することによって水素吸蔵合金を冷却・加熱した。その測定結果を、縦軸に水素吸蔵(放出)速度比をそして横軸に時間をした図3に示す。図3において、太線Aが本発明の水素吸蔵合金材料の場合であり、細線Bが比較例1の場合であり、破線Cが比較例2の場合である。図3から分かるように、本発明の水素吸蔵合金材料は水素の吸収・放出の速度が最も速い。この結果は熱伝導率の大きさの順と一致しており、熱電導率の向上が水素の吸蔵・放出速度の改善の主要因と考えられる。

【0021】水素に含まれている不純物ガスの水素吸蔵速度への影響を調べるために、高純度の場合と、不純物(4000ppm)含有の場合との水素吸蔵速度を上述の水素吸蔵時の条件にて、本発明の水素吸蔵合金材料および比較例2の未処理水素吸蔵合金粉末について測定した。その測定結果を図4に示す。実線Aが本発明の水素吸蔵合金材料の場合であり、破線Cが比較例2の場合である。図4から分かるように、不純物ガスが存在すると、水素吸蔵速度は遅くなるが、本発明の水素吸蔵合金材料は水素の吸蔵速度が比較例2よりも速い。これは、炭素・黒鉛多孔質体が不純物ガスのフィルターとして働き、水素吸蔵合金粉末の被毒を回避していると考えられる。

【0022】実施例2

実施例1の場合と同じ水素吸蔵合金粉末、石油ピッチおよびポリエスチルチップ用いて、水素吸蔵合金粉末の割合を30体積%一定とし、ポリエスチルチップ(直径:2μm、長さ:8μm)および石油ピッチの量を変えることで、空隙率を10~60体積%の範囲で変動させて、実施例1での製造方法によって水素吸蔵合金材料を製造した。それぞれの水素吸蔵合金材料について水素吸蔵速度(30°C、25気圧のH₂ガス圧)、熱伝導率およびガス透過速度を測定し、その結果を図5に示す。なお、水素吸蔵速度は水素吸蔵開始時の速度であり、図3での水素吸蔵速度比の立ち上がり傾きに相当する。また、図5ではガス透過速度比として空隙率60体積%の場合のガス透過速度で規格化した値(R/Rav60:%)である。

【0023】図5から分かるように、空隙率が大きくなるにつれて、ガス透過速度は大きくなるが、熱伝導率は小さくなる。そして、水素吸蔵速度は40体積%近傍が最も高い、山型カーブを描くように変動する。総合的に見て、特に、水素吸蔵速度を考慮して、空隙率は30~50体積%が好ましい。

実施例3

実施例1の場合と同じ水素吸蔵合金粉末および石油ピッチと形状を下記のように変えたポリエスチルチップ用いて、水素吸蔵合金粉末、石油ピッチおよびポリエスチル

チップの割合を30体積%、30体積%および40体積%一定とし、実施例1での製造方法によって水素吸蔵合金材料を製造した。

【0024】ポリエスチルチップの平均直径(μm)×長さ(μm):

1	×	4	
2	×	8	(実施例1)
3	×	12	
4	×	16	

10 それぞれの水素吸蔵合金材料について、水素の吸収・放出を実施例1と同じように水素吸蔵時に30°C、25気圧とし、水素放出時に60°C、1気圧としてこれを100回繰返して、初回および100回目の水素吸蔵速度を測定した。平均直径×長さが2μm×8μmの場合での水素吸蔵速度を100として、測定した値を水素吸蔵速度比として図6に示す結果が得られた。図6から明らかなように、100回の吸収放出繰返しで、水素吸蔵速度でポリエスチルチップの平均直径(2μm)のときが最も速い。また、平均直径が3μmを越えると、水素の吸収放出繰返しによって合金粉末の微粉化が生じことがある。これは、空隙が大きすぎて、水素吸蔵合金の膨張・収縮を低減できなくなつたためであろう。

【0025】さらに、得られた測定値を、空隙のアスペクト比(すなわち、ポリエスチルチップのアスペクト比)を基準に整理すると、図7に示す結果が得られる。この場合には、チップ(直径:2μm、長さ:8μm、アスペクト比:4)の時の水素吸蔵速度が最も速くて、これを100として、測定値を換算して示してある。アスペクト比を2~6とすれば、水素吸蔵速度は比較的高く、この範囲外では低下していることが分かる。

【0026】上述した実施例では、石油ピッチおよびポリエスチルチップを使用しているが、石炭タールおよびプラスチックチップなどを用いることも可能である。

【0027】

【発明の効果】以上説明したように、本発明に係る水素吸蔵合金材料は、空隙を有する炭素・黒鉛多孔質体で個々の水素吸蔵合金粉末を囲って所定の形状をそなえており、微粉化を抑制し、熱伝導率を高めかつ水素吸蔵・放出速度をも高めることができる。さらに、水素吸蔵合金

40 粉末の体積膨張・収縮歪み量は20%と大きいにもかかわらず、粉末の粒径が10~30μmと小さいので変形量は2~6μmと小さく、この変形を空隙を有する弹性体の海綿状多孔質体が吸収することになり、水素吸蔵合金材料(成形体)自体としての変形は極めて小さい。たとえ、水素吸蔵合金材料自体に変形が生じたとしても、収容容器との間に変形量相当の隙間を設けることによって、容器への応力負荷を回避することができる。そして、炭素・黒鉛は良電導体であって、直接に通電加熱が可能であり、水素放出時の加熱手段を簡素化できる。これらのことから、容器は単に水素を閉じ込める機能を有

するだけで良く、そのための最小限の板厚で容器を作れば良いことになる。したがって、例えば、定置式水素貯蔵用容器の場合に、水素貯蔵量 50 Nm^3 用の容器は数 kg程度まで軽量化が可能となる。

【図面の簡単な説明】

【図 1】本発明に係る水素吸蔵合金材料の拡大断面図である。

【図 2】本発明に係る水素吸蔵合金材料を製造する工程度のフローチャートである。

【図 3】水素吸収(放出)速度比を示すグラフである。

【図 4】水素ガスの純度に対応した水素吸収速度比を示すグラフである。

* 【図 5】水素吸蔵合金材料の空隙率と、水素吸収速度、熱伝導率およびガス透過速度比との関係を示すグラフである。

【図 6】ポリエステルチップの平均直径と水素吸収速度比との関係を示すグラフである。

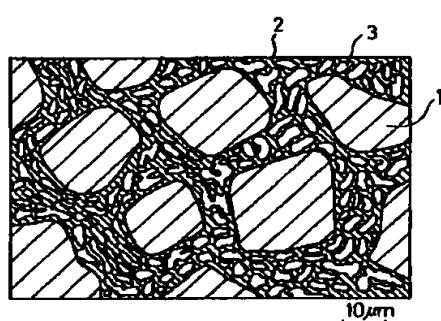
【図 7】ポリエステルチップのアスペクト比と水素吸収速度比との関係を示すグラフである。

【符号の説明】

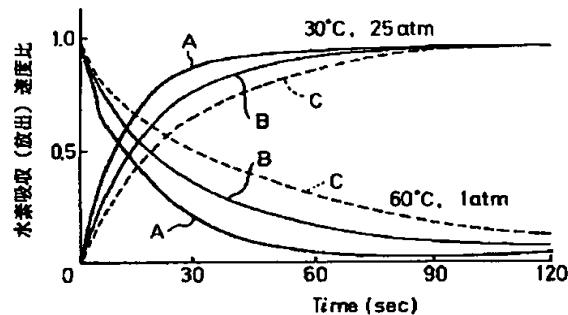
1 … 水素吸蔵合金粉末
10 2 … 炭素・黒鉛多孔質体(層)
3 … 空隙

*

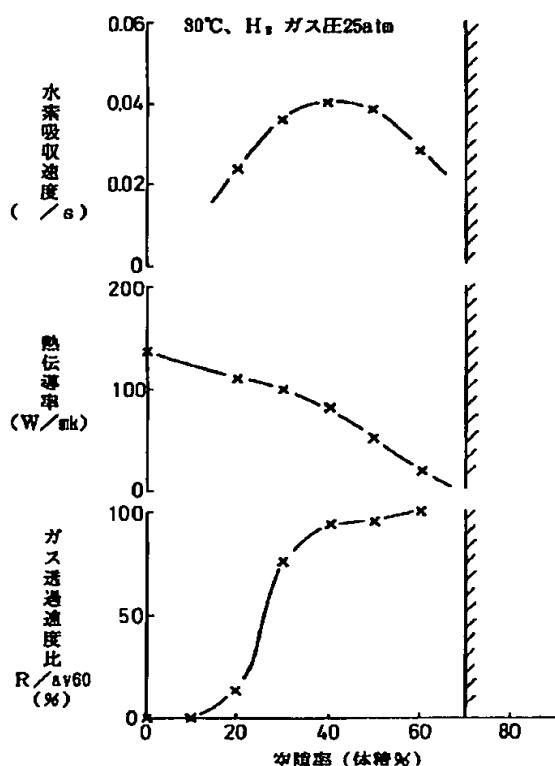
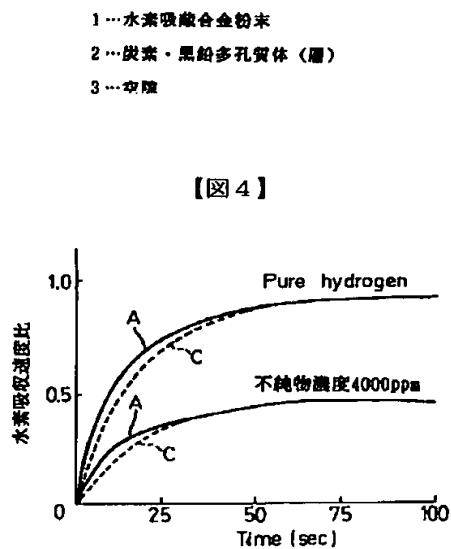
【図 1】



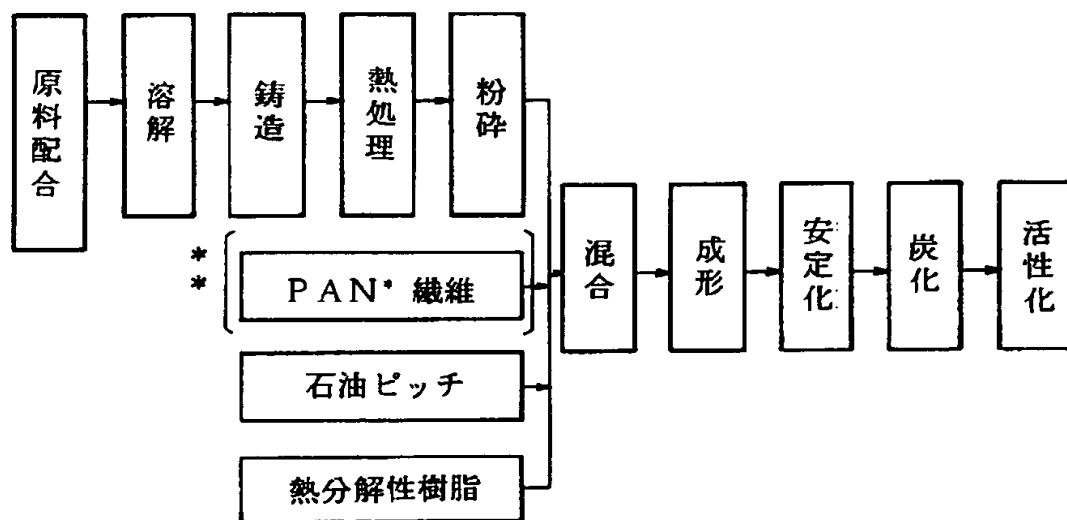
【図 3】



【図 5】



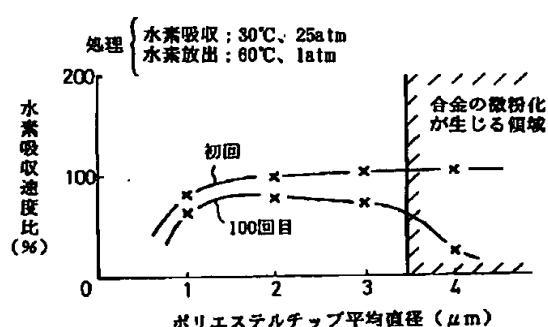
【図2】



* PAN: ポリアクリロニトリル

** 繊維強化時に添加

【図6】



【図7】

